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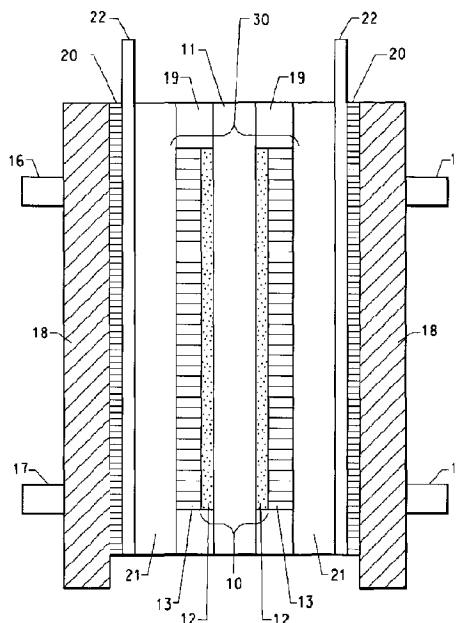
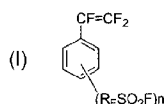
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(54) Title: TRIFLUOROSTYRENE CONTAINING COMPOUNDS, AND THEIR USE IN POLYMER ELECTROLYTE MEMBRANES



(57) Abstract: A monomer having the structure (I) wherein R<sub>F</sub> is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine; and n is 1 or 2. These monomers are used in the preparation of homopolymers and copolymers that are useful in preparing polymer electrolyte membranes. Electrochemical cells, such as fuel cells, containing these membranes are also described.



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# TITLE

## TRIFLUOROSTYRENE CONTAINING COMPOUNDS, AND THEIR USE IN POLYMER ELECTROLYTE MEMBRANES

### FIELD OF THE INVENTION

5           The present invention relates to a novel compound and its use in electrochemical cells as an electrolyte, and more particularly to the use of the compound as an electrolyte in fuel cells.

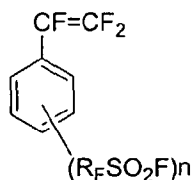
### BACKGROUND OF THE INVENTION

10           Electrochemical cells, such as fuel cells and lithium-ion batteries are known. Depending on the operating conditions, each type of cell places a particular set of requirements upon the electrolytes used in them. For fuel cells, this is typically dictated by the type of fuel, such as hydrogen or methanol, used to power the cell and the composition of the membrane used to separate the electrodes. Proton-exchange membrane fuel cells,  
15           powered by hydrogen as the fuel, could be run at higher operating temperatures than currently employed to take advantage of lower purity feed streams, improved electrode kinetics, better heat transfer from the fuel cell stack to improve its cooling. Waste heat is also employed in a useful fashion. However, if current fuel cells are to be operated at greater  
20           than 100 °C then they must be pressurized to maintain adequate hydration of typical proton-exchange membranes, such as DuPont Nafion® perfluorosulfonic acid membrane, to support useful levels of proton conductivity.

          There is an ongoing need to discover novel electrolytes that  
25           improve the performance of the latest generation of electrochemical cells, such as fuel cells and lithium-ion batteries, to develop new membrane materials that will maintain adequate proton conductivity at lower levels of hydration.

### SUMMARY OF THE INVENTION

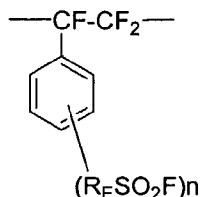
30           In a first aspect, the invention provides a monomer having the following structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine; and

5  $n$  is 1 or 2.

In a second aspect, the invention provides a homopolymer having the following structure:



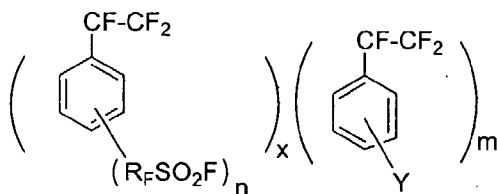
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10 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$n$  is 1 or 2, and

In a third aspect, the invention provides a copolymer selected from the group consisting of:

15 (a) a copolymer having the structure:



3

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

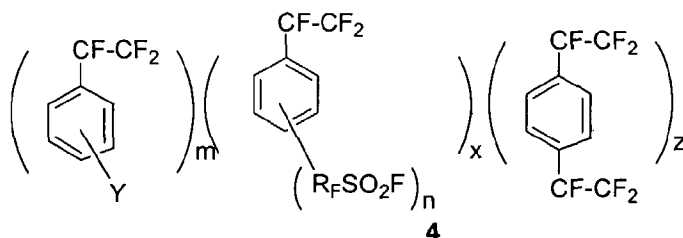
20  $Y$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

$n$  is 1 or 2,

25  $m$  and  $x$  are mole fractions wherein  $m$  is 0.01 to 0.99 and  $x$  is 0.99 to 0.01; and

$x+m = 1$

(b) a copolymer having the structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally

5 containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

10 n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

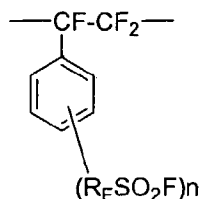
x is 0.99 to 0.01, and

z is 0.0001 to 0.10

$m + x + z = 1$ .

15 In a fourth aspect, the invention provides a polymer electrolyte membrane prepared from a homopolymer or copolymer selected from the group consisting of:

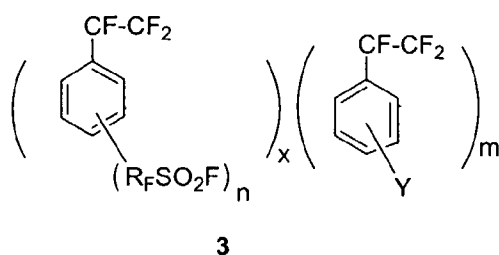
(a) a homopolymer having the structure:



20 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2;

(b) a copolymer having the structure:



5 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine,

10 and wherein the alkyl group comprises C1 to C10 carbon atoms,

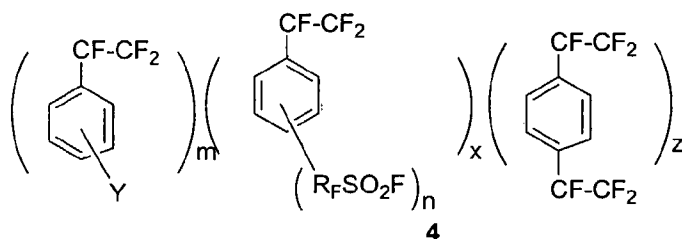
n is 1 or 2,

m and x are mole fraction wherein m is 0.01 to 0.99 and

x is 0.99 to 0.01; and

$x+m = 1$ ; and

15 (c) a copolymer having the structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

20 Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

25 m, x and z are mole fraction wherein m is 0.01 to 0.99,

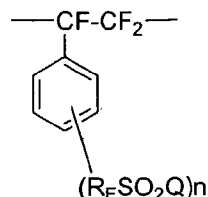
x is 0.99 to 0.01, and

z is 0.0001 to 0.10

$m + x + z = 1$ ; and mixtures thereof.

In the fourth aspect, the invention provides a polymer electrolyte membrane selected from the group consisting of:

5 (a) a membrane having the chemical structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$Q = OM, OH, NHSO_2R_F$ , wherein  $M = Li^+, Na, K$  or  $Cs$ ,

10  $n = 1$  or  $2$ ;

(b) a membrane having the chemical structure:

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally  
15 containing oxygen or chlorine,

$Y$  is  $H$ ; halogen such as  $Cl, Br, F$  or  $I$ ; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises  $C1$  to  $C10$  carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises  $C1$  to  $C10$  carbon atoms,

20  $Q = OM, OH, NHSO_2R_F$ , wherein  $M = Li^+, Na^+, K^+$  or  $Cs^+$ ,  
 $n$  is  $1$  or  $2$ ,

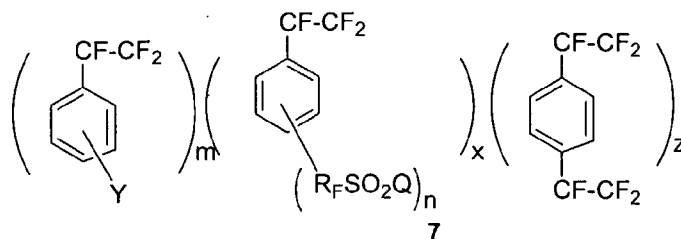
$m$  and  $x$  are mole fractions wherein  $m$  is  $0$  to  $0.99$ ,

$x$  is  $1$  to  $0.001$ , and

$x + m = 1$ ; and

25

(c) a membrane having the chemical structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

Q = OM, OH,  $\text{NHSO}_2R_F$ , wherein  $M = \text{Li}^+, \text{Na}^+, \text{K}^+$  or  $\text{Cs}^+$ ,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99 ,

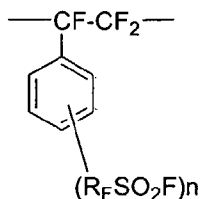
x is 0.99 to 0.01,

z is 0.0001 to 0.10, and

$m + x + z = 1$

In a fifth aspect, the invention provides a membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the membrane is prepared from a homopolymer or copolymer selected from the group consisting of:

(a) a homopolymer having the structure:

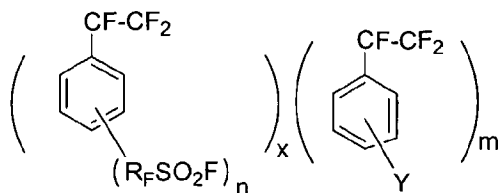


wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2;

(b) a copolymer having the structure:





3

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

- Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

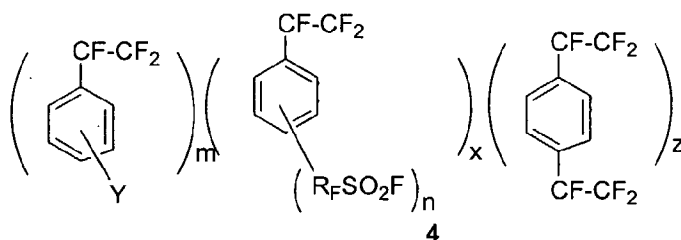
n is 1 or 2,

m and x are mole fractions wherein m is 0.01 to 0.99,

- x is 0.99 to 0.01; and

$x+m = 1$ ; and

(c) a copolymer having the structure:



4

- wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

- Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01, and

z is 0.0001 to 0.10

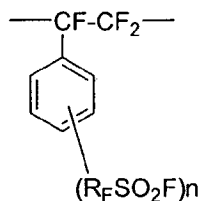
- m + x + z = 1; and mixtures thereof.

In the fifth aspect, the membrane electrode assembly comprises a polymer electrolyte membrane further comprising a porous support.

In the fifth aspect, the membrane electrode assembly further comprises at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the membrane. It also further comprises at least one gas diffusion backing. Alternately, the membrane electrode assembly further comprises a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

In a sixth aspect, the invention provides an electrochemical cell, such as a fuel cell, comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the membrane is prepared from a homopolymer or copolymer selected from the group consisting of:

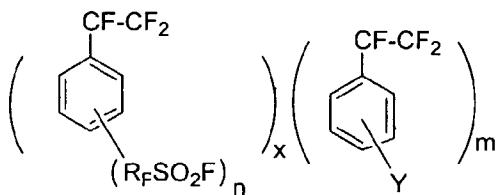
(a) a homopolymer having the structure:



2

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,  
n is 1 or 2;

(b) a copolymer having the structure:



3

25

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

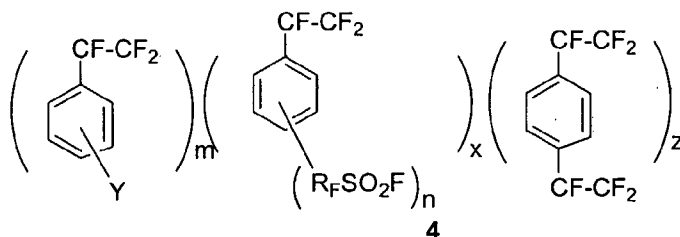
n is 1 or 2,

m and x are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01,

x+m = 1, and

(c) a copolymer having the structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01,

z is 0.0001 to 0.10, and

m + x + z = 1; and mixtures thereof.

In the sixth aspect, the invention provides a fuel cell comprising a polymer electrolyte membrane further comprising a porous support.

In the sixth aspect, the fuel cell further comprises at least one electrode prepared from an electrocatalyst containing composition, e.g., an anode and a cathode, present on the first and second surfaces of the polymer electrolyte membrane. It also further comprises at least one gas diffusion backing. Alternately, the membrane electrode assembly further comprises a gas diffusion electrode present on the first and second

surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

In the sixth aspect, the fuel cell further comprises a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode. The fuel is in the liquid or vapor phase. Some suitable fuels include hydrogen, alcohols such as methanol and ethanol; ethers such as diethyl ether, etc.

#### BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of a single cell assembly.

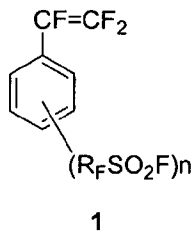
Figure 2 is a schematic illustration of the lower fixture of a four-electrode cell for in-plane conductivity measurement.

#### DETAILED DESCRIPTION OF THE INVENTION

The monomers of the invention that are small molecules may be used to prepare homopolymers or copolymers that are useful as electrolytes in the preparation of the solid polymer electrolyte membranes. These polymer electrolyte membranes are used to make catalyst-coated membranes that are a component of fuel cells. These homopolymers or copolymers are also useful as electrolytes in other electrochemical cells, such as batteries, chloralkali cells, electrolysis cells, sensors, electrochemical capacitors, and modified electrodes.

#### Monomer:

The monomers of the invention have the following structure:

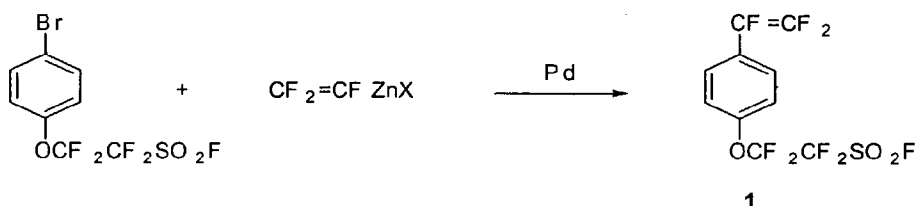


wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine, such as  $(CF_2)_r$  wherein  $r = 1$  to  $20$ ,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to  $6$ ,  $CF(CF_3)O)_rCF_2CF_2$  wherein  $r = 1$  to  $8$ , and more typically  $(CF_2)_r$  wherein  $r = 1$  to  $8$ ,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to  $2$ ,  $CF(CF_3)O)_rCF_2CF_2$  wherein  $r = 1$  to  $2$ ; and

n is 1 or 2, more typically n is 1.

#### A. Synthesis of monomers

Monomer having structure **1** was prepared by the Pd catalyzed reaction of a trifluorovinyl zinc reagent with aryl bromide, which was disclosed in Feiring, et al, J. Fluorine Chem. 105, 129, 2000. The vinyl zinc reagent was made from the reaction of  $\text{CF}_2=\text{CFBr}$  and zinc powder in DMF (Burton et al, JOC 53, 2714, 1988).



Other monomers such as trifluorostyrene and 1,4-bis(trifluorostyrene) were made in similar fashion according to Burton's method. Alternatively, the monomers can be prepared by reaction of iodohalobenzenes with  $\text{IR}_\text{F}\text{SO}_2\text{F}$  in the presence of copper powder to give the coupling products  $\text{XC}_6\text{H}_4\text{R}_\text{F}\text{SO}_2\text{F}$ , followed by a palladium catalyzed coupling reaction with  $\text{CF}_2=\text{CFZnX}$ . A third method includes first adding  $\text{CF}_2\text{ClCF}_2\text{I}$  to iodo- or bromobenzenes to give  $\text{CF}_2\text{ClCFClC}_6\text{H}_4\text{X}$  wherein  $\text{X} = \text{I}, \text{Br}$ , and then coupling with  $\text{IR}_\text{F}\text{SO}_2\text{F}$  in the presence of copper powder to produce the coupled product,  $\text{CF}_2\text{ClCFClC}_6\text{H}_4\text{R}_\text{F}\text{SO}_2\text{F}$ , which was treated with Zn to produce the desired monomer  $\text{CF}_2=\text{CFC}_6\text{H}_4\text{R}_\text{F}\text{SO}_2\text{F}$ .  $\text{CF}_2\text{ClCF}_2\text{I}$  also reacts with diiodo- or dibromobenzenes to give  $\text{CF}_2\text{ClCFClC}_6\text{H}_3\text{X}_2$  wherein  $\text{X} = \text{Br}, \text{I}$ , which may be coupled with  $\text{IR}_\text{F}\text{SO}_2\text{F}$  and copper powder resulting in  $\text{CF}_2\text{ClCFClC}_6\text{H}_3(\text{R}_\text{F}\text{SO}_2\text{F})_2$ . Finally, dechlorination of  $\text{CF}_2\text{ClCFClC}_6\text{H}_3(\text{R}_\text{F}\text{SO}_2\text{F})_2$  with zinc gives  $\text{CF}_2=\text{CFC}_6\text{H}_3(\text{R}_\text{F}\text{SO}_2\text{F})_2$ .

#### Homopolymers and Copolymers:

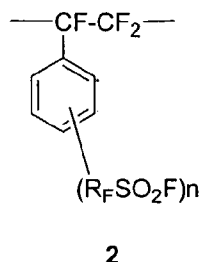
These monomers are used to prepare homopolymers and copolymers using the following procedure: Homo- and copolymerization of **1** may be conducted by neat polymerization, solution polymerization, suspension polymerization, or emulsion polymerization. Typical initiators such as Lupersol® 11 and perfluoroacyl peroxide were used in suspension polymerization or solution polymerization. In an aqueous polymerization, inorganic peroxides such as potassium persulfates (KPS) and ammonium persulfate (APS) obtained from Aldrich, Milwaukee, WI) were used as an initiator, or fluorinated

organic salts such as ammonium perfluorooctanoate and fluorinated alkane sulfonates, or non-fluorinated surfactants such as dodecylamine hydrochloride salt were used as surfactants. Monomers represented by structure 1 were typically used in aqueous emulsion polymerization.

- 5 Molecular weight of polymers can be controlled by addition of chain transfer agents such as halocarbons,  $\text{CHCl}_3$ , fluorinated iodides and bromides, MeOH, ethers esters and alkanes. Polymers were isolated by coagulation. The polymers have high thermal stability and may be pressed into thin films. The polymer also dissolved in certain solvents
- 10 such as trifluorotoluene and 2,5-dichlorotrifluorotoluene. Thin films may also be cast from these polymer solutions. Slightly crosslinked polymers such as those having the structure 4 have improved mechanical properties and reduced excess water uptake.

The resulting homopolymer formed by the above procedure has the following structure:

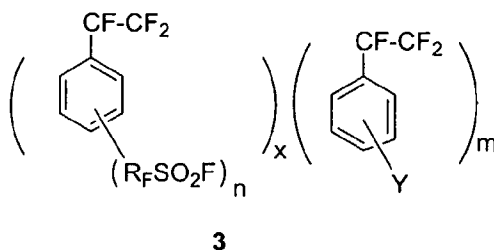
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- wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine, such as  $(\text{CF}_2)_r$  wherein  $r = 1$  to 20,  $(\text{CF}_2\text{CF}_2)_r\text{OCF}_2\text{CF}_2$  wherein  $r = 0$  to 6,  $\text{CF}(\text{CF}_3)\text{O}_r\text{CF}_2\text{CF}_2$  wherein  $r = 1$  to 8, and more typically  $(\text{CF}_2)_r$  wherein  $r = 1$  to 8,  $(\text{CF}_2\text{CF}_2)_r\text{OCF}_2\text{CF}_2$  wherein  $r = 0$  to 2,  $\text{CF}(\text{CF}_3)\text{O}_r\text{CF}_2\text{CF}_2$  wherein  $r = 1$  to 2;
- $n$  is 1 or 2, more typically  $n$  is 1; and

The resulting copolymer formed using the above procedure are represented by the structure:

25



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine, such as  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6,  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 8, and more typically  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2,  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 2 ;

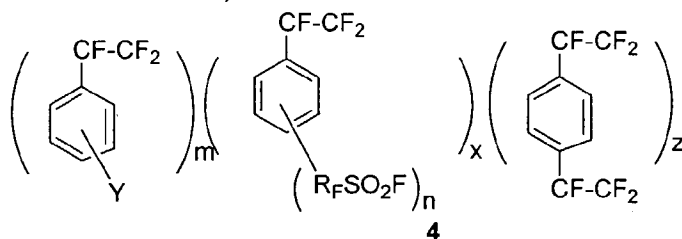
Y is H; halogen such as F, Cl, Br, or I; linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, such as  $C_nF_{2n+1}$  and  $C_nH_{2n+1}$ , wherein  $n$  is 1 to 10, more typically  $C_qF_{2q+1}$  wherein  $q$  is 1 to 6; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, such as  $CF_3(CF_2)_qO(CF_2CF_2)_q$  wherein  $q = 1$  to 5,  $CF_3CF_2CF_2(OCF_2CF_3)_q$  wherein  $q = 1$  to 5; and more typically  $CF_3(CF_2)_qOCF_2CF_2$  wherein  $q = 1$  to 2,  $CF_3CF_2CF_2(OCF_2CF_3)_q$  wherein  $q = 1$  to 3;

n is 1 or 2, more typically 1;

m and x are mole fractions wherein m is 0 to 0.99, more typically 0.1 to 0.4;

x is 1 to 0.001; more typically 0.9 to 0.6; and

$x + m = 1$ ; and



20

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine, such as  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6,  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 8, and more typically  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2,  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 2 ; and

Y is H; halogen such as F, Cl, Br, or I; linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, such as  $C_nF_{2n+1}$  and  $C_nH_{2n+1}$ , wherein  $n$  is 1 to 10, more typically  $C_qF_{2q+1}$  wherein  $q$  is 1 to 6; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, such as  $CF_3(CF_2)_qO(CF_2CF_2)_q$  wherein  $q = 1$  to 5,  $CF_3CF_2CF_2(OCF_2CF_3)_q$  wherein  $q = 1$  to 5; and more

typically  $\text{CF}_3(\text{CF}_2)_q\text{OCF}_2\text{CF}_2$  wherein  $q = 1$  to  $2$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2(\text{OCF}_2\text{CF}_3)_q$  wherein  $q = 1$  to  $3$ ;

$n$  is  $1$  or  $2$ , more typically  $1$ ;

$m$ ,  $x$  and  $z$  are mole fractions wherein  $m$  is  $0.1$  to  $0.8$ , more typically

5  $0.2$  to  $0.6$ ;

$x$  is  $0.2$  to  $0.9$ , more typically  $0.4$  to  $0.8$ ; and

$z$  is  $0.001$  to  $0.05$ , more typically  $0.002$  to  $0.01$ .

#### Membrane:

The homopolymer and copolymers can be cast into thin films from  
10 their solutions. Typically, THF, trifluorotoluene were used as solvents. The  
cast films were transparent and flexible. The films also may also be made  
by thermally pressing at  $200$  to  $250^\circ\text{C}$ . The films may be hydrolyzed with  
bases such as  $\text{MOH}$ ,  $\text{M}_2\text{CO}_3$  wherein  $\text{M} = \text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Cs}^+$ , or  $\text{MOH}$  in  
a mixture of  $\text{MeOH}$ ,  $\text{DMSO}$  and water. The hydrolysis is typically carried  
15 out at room temperature to  $373^\circ\text{F}$ , preferably at room temperature to  
 $323^\circ\text{F}$ . Treatment of polymeric salts with acids such as  $\text{HNO}_3$  gave  
polymeric acids. Polymers represented by structures **2**, **3** and **4** may be  
converted to the corresponding sulfonimide by reaction with  $\text{CF}_3\text{SO}_2\text{NH}_2$   
and base.

20 The ionomers of homopolymers and copolymers identified above  
may be imbibed into a porous support to form a polymer electrolyte  
membrane having improved mechanical properties and dimensional  
stability. These membranes are capable of operating at a temperature of  
above  $100^\circ\text{C}$ . Ionomers may have  $5\%$  to  $99.9\%$  of membrane weight,  
25 typically,  $20$  to  $98\%$ , more typically  $50$  to  $90\%$ .

#### Porous Support:

The porous support of the membrane may be made from a wide  
range of components. The porous support of the present invention may be  
made from a hydrocarbon such as a polyolefin, e.g., polyethylene,  
30 polypropylene, polybutylene, copolymers of those materials, and the like.  
Perhalogenated polymers such as polychlorotrifluoroethylene may also be  
used. For resistance to thermal and chemical degradation, the support  
preferably is made of a highly fluorinated polymer, most preferably  
perfluorinated polymer.

35 For example, the polymer for the porous support can be a  
microporous film of polytetrafluoroethylene (PTFE) or a copolymer of  
tetrafluoroethylene with other perfluoroalkyl olefins or with perfluorovinyl  
ethers. Microporous PTFE films and sheeting are known which are



suitable for use as a support layer. For example, U. S. Pat. No. 3,664,915 discloses uniaxially stretched film having at least 40% voids. U.S. Pat. Nos. 3,953,566, 3,962,153 and 4,187,390 disclose porous PTFE films having at least 70% voids.

5           Alternatively, the porous support may be a fabric made from fibers of the support polymers discussed above woven using various weaves such as the plain weave, basket weave, leno weave, or others. A membrane suitable for the practice of the invention can be made by coating the porous support fabric with the compound of the invention to  
10       form a composite membrane. To be effective the coating must be on both the outside surfaces as well as distributed through the internal pores of the support. This may be accomplished by impregnating the porous support with a solution or dispersion of the polymer suitable for the practice of the invention using a solvent that is not harmful to the polymer or the support,  
15       and under impregnation conditions that can form a thin, even coating of the polymer on the support. The support with the solution/dispersion is dried to form the membrane. If desired, thin films of the ion exchange polymer can be laminated to one or both sides of the impregnated porous support to prevent bulk flow through the membrane that can occur if large  
20       pores remain in the membrane after impregnation.

          It is preferred for the compound to be present as a continuous phase within the membrane.

          Other forms of the solid polymer electrolyte membrane include the PTFE yarn embedded type and the PTFE fibril dispersed type, wherein the  
25       PTFE fibril is dispersed in the ion exchange resin as disclosed in 2000 Fuel Cell Seminar (10/30 to 11/2, 2000, Portland, Oregon) Abstracts, p-23. Electrochemical Cell:

          As shown in Figure 1, an electrochemical cell, such as a fuel cell, comprises a catalyst-coated membrane (CCM) **(10)** in combination with at  
30       least one gas diffusion backing (GDB) **(13)** to form an unconsolidated membrane electrode assembly (MEA). The catalyst-coated membrane **(10)** comprises an ion exchange polymer membrane **(11)** discussed above and catalyst layers or electrodes **(12)** formed from an electrocatalyst coating composition. The fuel cell is further provided with an inlet **(14)** for  
35       fuel, such as liquid or gaseous alcohols, e.g. methanol and ethanol; or ethers such as diethyl ether, etc., an anode outlet **(15)** a cathode gas inlet **(16)** a cathode gas outlet **(17)** aluminum end blocks **(18)** tied together with tie rods (not shown), a gasket for sealing **(19)** an electrically insulating

layer (20) and graphite current collector blocks with flow fields for gas distribution (21) and gold plated current collectors (22).

The fuel cell utilizes a fuel source that may be in the liquid or gaseous phase, and may comprise hydrogen, an alcohol or ether.

- 5 Typically a methanol/water solution is supplied to the anode compartment and air or oxygen supplied to the cathode compartment.

Catalyst Coated Membrane (CCM):

- 10 A variety of techniques are known for CCM manufacture which apply an electrocatalyst coating composition similar to that described above onto the solid fluorinated polymer electrolyte membrane. Some known methods include spraying, painting, patch coating and screen, decal, pad or flexographic printing.

- 15 In one embodiment of the invention, the MEA (30), shown in Figure 1, may be prepared by thermally consolidating the gas diffusion backing (GDB) with a CCM at a temperature of under 200°C, preferably 140-160°C. The CCM may be made of any type known in the art. In this embodiment, an MEA comprises a polymer electrolyte (SPE) membrane with a thin catalyst- binder layer disposed thereon. The catalyst may be supported (typically on carbon) or unsupported. In one method of  
20 preparation, a catalyst film is prepared as a decal by spreading the catalyst ink on a flat release substrate such as Kapton® polyimide film (available from the DuPont Company). After the ink dries, the decal is transferred to the surface of the SPE membrane by the application of pressure and heat, followed by removal of the release substrate to form a  
25 catalyst coated membrane (CCM) with a catalyst layer having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer is applied directly to the membrane, such as by printing, and then the catalyst film is dried at a temperature not greater than 200°C.

Membrane Electrode Assembly:

- 30 The CCM, thus formed, is then combined with a GDB to form the MEA (30). The MEA is formed, by layering the CCM and the GDB, followed by consolidating the entire structure in a single step by heating to a temperature no greater than 200°C, preferably in the range of 140-160°C, and applying pressure. Both sides of the MEA can be formed in  
35 the same manner and simultaneously. Also, the composition of the catalyst layer and GDB could be different on opposite sides of the membrane. Alternately, the membrane electrode may be formed by placing gas diffusion electrode each surface of the polymer electrolyte

membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition. The electrocatalyst composition may comprise the homopolymers or copolymers of the invention as a binder in the composition.

The invention is illustrated in the following examples.

### EXAMPLES

#### Liquid Conductivity Measurement

The conductivity of a liquid is measured using a cell capable of handling corrosive samples at elevated temperature with volumes as small as 800  $\mu\text{L}$ . Two coil electrodes are formed 25 mm apart by wrapping 0.38 mm diameter platinum wires five times around one end of a 5.14 mm diameter Macor® machinable glass ceramic rod (Corning Inc., Corning, NY) and insulating the remainder of the wire leads with heat-shrink PTFE tubing. The sample is loaded into a 9 mm outside diameter x 6.8 mm inside diameter x 178 mm length glass tube and the rod is inserted so that the electrodes are completely immersed in the sample. The tube is placed into a forced-convection thermostated oven for heating. The real part of the AC impedance,  $R_s$ , is measured at a frequency of 1 kHz using a potentiostat/frequency response analyzer (PC4/750™ with EIS software, Gamry Instruments, Warminster, PA). The phase angles are typically less than 2 degrees, which indicates that the measurement is unaffected by capacitive contributions from the electrode interfaces. The cell constant,  $K$ , is determined by measuring the real part of the impedance,  $R_c$ , at a frequency of 10 kHz using a NIST traceable potassium chloride conductivity calibration standard for nominal 0.1 S/cm (0.1027 S/cm actual) and calculating as

$$K = R_c \times 0.1027 \text{ S/cm} \times (1 + \Delta T \times 0.02 \text{ } ^\circ\text{C}^{-1})$$

where  $\Delta T$  is the difference between the temperature of the calibration standard,  $T_m$ , and 25  $^\circ\text{C}$  ( $\Delta T = T_m - 25$ ). The cell constant is typically close to 12  $\text{cm}^{-1}$ . The conductivity,  $\kappa$ , of the sample is then calculated as

$$\kappa = K / R_s$$

### Through-Plane Conductivity Measurement

The through-plane conductivity of a membrane is measured by a technique in which the current flows perpendicular to the plane of the membrane. The lower electrode is formed from a 12.7 mm diameter stainless steel rod and the upper electrode is formed from a 6.35 mm diameter stainless steel rod. The rods are cut to length, and their ends are polished and plated with gold. A stack is formed consisting of lower electrode / GDE / membrane / GDE / upper electrode. The GDE (gas diffusion electrode) is a catalyzed ELAT® (E-TEK Division, De Nora North America, Inc., Somerset, NJ) comprising a carbon cloth with microporous layer, platinum catalyst, and 0.6-0.8 mg/cm<sup>2</sup> Nafion® application over the catalyst layer. The lower GDE is punched out as a 9.5 mm diameter disk, while the membrane and the upper GDE are punched out as 6.35 mm diameter disks to match the upper electrode. The stack is assembled and held in place within a block of Macor® machinable glass ceramic (Corning Inc., Corning, NY) that has a 12.7 mm diameter hole drilled into the bottom of the block to accept the lower electrode and a concentric 6.4 mm diameter hole drilled into the top of the block to accept the upper electrode. A force of 270 N is applied to the stack by means of a clamp and calibrated spring. This produces a pressure of 8.6 MPa in the active area under the upper electrode, which insures a low impedance ionic contact between the GDE's and the membrane. The fixture is placed in a forced-convection thermostated oven for heating. The real part of the AC impedance of the fixture containing the membrane,  $R_s$ , is measured at a frequency of 100 kHz using a potentiostat/frequency response analyzer (PC4/750™ with EIS software, Gamry Instruments, Warminster, PA). The fixture short,  $R_f$ , is also determined by measuring the real part of the AC impedance at 100 kHz for the fixture and stack assembled without a membrane sample. The conductivity,  $\kappa$ , of the membrane is then calculated as

$$\kappa = t / ( (R_s - R_f) \times 0.317 \text{ cm}^2 ),$$

where  $t$  is the thickness of the membrane in cm.

### In-Plane Conductivity Measurement

The in-plane conductivity of a membrane is measured under conditions of controlled relative humidity and temperature by a technique in which the current flows parallel to the plane of the membrane. A four-

electrode technique is used similar to that described in an article entitled "Proton Conductivity of Nafion<sup>®</sup> 117 As Measured by a Four-Electrode AC Impedance Method" by Y. Sone et al., J. Electrochem. Soc., 143,1254 (1996), which is herein incorporated by reference. Referring to Figure 2, a lower fixture (40) is machined from annealed glass-fiber reinforced PEEK to have four parallel ridges (41) containing grooves that support and hold four 0.25 mm diameter platinum wire electrodes. The distance between the two outer electrodes is 25 mm, while the distance between the two inner electrodes is 10 mm. A strip of membrane is cut to a width between 10 and 15 mm and a length sufficient to cover and extend slightly beyond the outer electrodes, and placed on top of the platinum electrodes. An upper fixture (not shown), which has ridges corresponding in position to those of the bottom fixture, is placed on top and the two fixtures are clamped together so as to push the membrane into contact with the platinum electrodes. The fixture containing the membrane is placed in a small pressure vessel (pressure filter housing), which is placed in a forced-convection thermostated oven for heating. The temperature within the vessel is measured by means of a thermocouple. Water is fed from a calibrated Waters 515 HPLC pump (Waters Corporation, Milford, MA) and combined with dry air fed from a calibrated mass flow controller (200 sccm maximum) to evaporate the water within a coil of 1.6 mm diameter stainless steel tubing inside the oven. The resulting humidified air is fed into the inlet of the pressure vessel. The total pressure within the vessel (100 to 345 kPa) is adjusted by means of a pressure-control letdown valve on the outlet and measured using a capacitance manometer (Model 280E, Setra Systems, Inc., Boxborough, MA). The relative humidity is calculated assuming ideal gas behavior using tables of the vapor pressure of liquid water as a function of temperature, the gas composition from the two flow rates, the vessel temperature, and the total pressure. Referring to Figure 2, the slots (42) in the lower and upper parts of the fixture allow access of humidified air to the membrane for rapid equilibration with water vapor. Current is applied between the outer two electrodes while the resultant voltage is measured between the inner two electrodes. The real part of the AC impedance (resistance) between the inner two electrodes,  $R$ , is measured at a frequency of 1 kHz using a potentiostat/frequency response analyzer (PC4/750<sup>™</sup> with EIS software, Gamry Instruments, Warminster, PA). The conductivity,  $\kappa$ , of the membrane is then calculated as

$$\kappa = 1.00 \text{ cm} / (R \times t \times w),$$

where  $t$  is the thickness of the membrane and  $w$  is its width (both in cm).

Example 1:

- 5 p-CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was prepared using the following procedure:

A 1000 mL two necked flask fitted with rubber septa, a magnetic stirring bar, vented connector tube and a dry ice condenser vented to a nitrogen purge tube bubbler was charged with 45 g(0.69 mol) of acid-washed Zn and 500-mL of DMF at room temperature. CF<sub>2</sub>=CFBr was slowly added as a gas via the vented connector tube and allowed to condense at the dry ice to a suspension of Zn and DMF mixture in the flask. After addition of 2 mL of bromine, an exothermic reaction occurred and the mixture was stirred at room temperature for 2 hrs, during which 15 99.1 g (0.616 mol) of CF<sub>2</sub>=CFBr were added, and then stirred at 65°C for 1.5 hrs to give CF<sub>2</sub>=CFZnX solution.

A 1 L three necked flask fitted with a magnetic stirring bar, and a cold water condenser was charged with 6.0 g of Pd(PPh<sub>3</sub>)<sub>4</sub>, and then 560 mL of (CF<sub>2</sub>=CF)ZnX solution prepared as described above was transferred via a cannula to the reaction flask. 115 g (0.324 mol) of p-Br-(C<sub>6</sub>H<sub>4</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F were added via a syringe and the reaction mixture was heated to 75° C for 10 hours. The condenser was replaced with a distillation head and distilled at 0.30-1.8 mmHg to a receiver that was cooled with dry ice. About 500 mL of a clear light yellow liquid was 25 obtained. This clear light yellow liquid was poured into water and the lower layer separated, washed with two times its volume of ice cold water, and then with a brine solution to recover 101.56 g. of crude product. Distillation gave 99 g (86%) of pure product, bp 57-61°C/0.5 mmHg. <sup>19</sup>F NMR: +43.8 (m, 1F), -82.0 (s, 2F), -99.7(dd, J = 67.8 Hz, J = 34 Hz, 1F), -112.0 (s, 2F), -114.4 (dd, J = 109.3 Hz, J = 67.8 Hz, 1F), -177.4 (dd, J = 109.3 Hz, J = 34 Hz, 1F). <sup>1</sup>H NMR: 7.6 (d, J = 8 Hz, 2H), 7.2 (d, J = 8 Hz, 2H).

Example 2:

- 35 CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was polymerized using ammonium persulfate (APS):

A 250 mL three necked round bottomed flask, fitted with a rubber septa, cold-water condenser with a N<sub>2</sub> outlet/inlet and bubbler, a magnetic stirring bar, and thermocouple, was charged with 50 mL of deionized

water and 4.8 mL 20 wt.% C8 solution (aq). The solution was bubbled with N<sub>2</sub> for 30 min. then 7.2 g (20.2 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F were added to the flask via a syringe under N<sub>2</sub>, and then ultrasonicated for 5 min. After heating to 50° C, 50 mg of APS in 2 mL of water were added and the resulting mixture was stirred at 50°C over weekend, and then an additional 10 mg of APS in 1 mL of water were added. Stirring of the mixture was continued for 14 hrs and then the mixture was frozen. After melting, the mixture was treated with 15 ml of 10% HNO<sub>3</sub> at 90°C for 1.5 hrs, then cooled to RT. The resulting solids were filtered and washed with water three times and further dried at 105°C under vacuum/N<sub>2</sub> for 4 hrs to give 5.41 g of polymer, which was soluble in THF. <sup>1</sup>H NMR(THF-d<sub>8</sub>): 6.0-7.8 ppm. <sup>19</sup>F NMR: +40.2 (s, 1F), -84.6 (m, 2F), -107 to -133 (m, 2F), -114.8 (s, 2F), -175 to -178 (m, 1F). Analysis: calcd for C<sub>10</sub>H<sub>4</sub>F<sub>8</sub>SO<sub>3</sub>: C, 33.71; H, 1.13; F, 42.70; S, 8.98. Found: C, 33.84; H, 0.93; F, 42.7; S, 8.98. Mw = 9.39x10<sup>5</sup>, Mn = 1.05x10<sup>5</sup>. DSC indicated the polymer had a Tg of 165°C. TGA indicated decomposition temperature was 300°C and 10% weight loss was 340°C in air when heated at 10°C/min.

Example 3:

CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was polymerized using the following procedure:

A 500 mL three necked round bottomed flask, fitted with a rubber septa, cold water condenser with a N<sub>2</sub> outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 100 mL of deionized water and 8.0 mL of 20 wt.% C8 solution (aq). The solution was bubbled with N<sub>2</sub> for 30 min. then 14.4 g (40.4 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F were added to the flask via a syringe under N<sub>2</sub> and the mixture ultrasonicated for 5 min. After heating to 55° C, 57 mg of KPS in 2 mL of water were added and the resulting mixture was stirred at 55°C for 26 hrs. An additional 28 mg of KPS in 2 mL of water were then added. Stirring of the mixture was continued for 22 hrs and the mixture was frozen. After melting, the mixture was treated with 50 ml of 10% HNO<sub>3</sub> at 90°C for 1.5 hrs, then cooled to RT. The resulting solids were filtered and washed with DI water three times to give a fine off-white polymer with some larger solids. The solids were slurried in methanol, filtered and air-dried. After air-drying overnight, 15.84 g of a white solid were recovered. The sample was further dried at 100°C under vacuum/N<sub>2</sub> overnight and 12.0 g. of sample having Mw = 8.44x10<sup>5</sup> and Mn = 2.02x10<sup>5</sup> were recovered.

#### Example 4

$\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  was polymerized using APS at 80°C and the following procedure:

- A 100 mL three necked round bottomed flask, fitted with a rubber septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 40 mL of deionized water and 3.8 mL 20 wt.% C8 solution (aq). The solution was bubbled with  $\text{N}_2$  for 75 min and then 5.6 g (15.7 mmol) of  $\text{F}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  were added to the flask via a syringe under  $\text{N}_2$ . After heating to 80° C, 4 mg of APS in 1 mL of water were added to the flask with stirring every hour for 11 hours. The mixture was then frozen in the flask. After melting, the mixture was treated with 10 ml of 10%  $\text{HNO}_3$  at 90°C for 1.5 hrs, and then cooled to RT. The resulting solids were filtered and washed with water three times and further dried at 105°C under vacuum/ $\text{N}_2$  for 5 hrs to give 4.98 g of polymer (88.9%) having a  $M_w = 4.44 \times 10^5$  and a  $M_n = 7.16 \times 10^4$

#### Example 5

$\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  was prepared in the presence of  $\text{CHCl}_3$  using APS  $\text{CHCl}_3$  at 80°C, and the following procedure:

- A 100 mL three necked round bottomed flask, fitted with rubber septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 40 mL of deionized water and 3.8 mL 20 wt.% C8 aqueous solution. The solution was bubbled with  $\text{N}_2$  for 75 min., followed by the addition of 5.6 g (15.7 mmol) of  $\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and 10  $\mu\text{l}$  of  $\text{CHCl}_3$  via a syringe under  $\text{N}_2$ . After heating to 80° C, 4 mg of APS in 1 mL of water were added to the flask with stirring every hour for 11 hours. The mixture was then frozen. After melting, the mixture was treated with 10 ml of 10%  $\text{HNO}_3$  at 90°C for 1.5 hrs, and then cooled to RT. The resulting solids were filtered and washed with water three times and further dried at 110°C under vacuum/ $\text{N}_2$  for 5 hrs to give 4.46 g of polymer (79.6%) having a  $M_w = 2.04 \times 10^5$  and an  $M_n = 5.62 \times 10^4$

#### Example 6

- p- $\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  polymer was prepared in the presence of  $\text{I}(\text{CF}_2)_6\text{I}$  using APS at 80°C, and the following procedure:

A 100 mL three necked round bottomed flask, fitted with a rubber septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 40 mL of deionized water



and 3.8 mL 20 wt.% C8 solution (aq). The solution was bubbled with N<sub>2</sub> for 75 min, and then 5.6 g (15.7 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 35 mg of I(CF<sub>2</sub>)<sub>6</sub>I were added to the flask via a syringe under N<sub>2</sub>. After heating to 80° C, 4 mg of APS in 1 mL of water were added to the flask with stirring every hour for 11 hours. The mixture was then frozen. After melting, the mixture was treated with 10 ml of 10% HNO<sub>3</sub> at 90°C for 1.5 hrs, and then cooled to RT. The resulting solids were filtered and washed with water three times and further dried at 105°C under vacuum/N<sub>2</sub> for 5 hrs to give 4.18 g of (79.1%) of polymer having a Mw = 5.39x10<sup>5</sup> and Mn = 1.10x10<sup>4</sup>

#### Example 7

p-CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was copolymerized with trifluorostyrene using the following procedure:

A three-necked clean flask, fitted with an N<sub>2</sub> inlet/outlet, a magnetic stirring bar and a thermocouple, was charged with 25 mL of deionized water and 2.1 mL of 20% C8 aqueous solution. The solution was bubbled with N<sub>2</sub> for 30 min. 2.9 g of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 1.3 g (8.2 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>5</sub> were added to the flask via a syringe under N<sub>2</sub> purge. After heating to 55°C (temperature control is very important!), 52 mg of Potassium persulfate (KPS) in 2 mL of deionized water were added via a syringe and the flask was kept at 55°C for 24 hrs. An additional 15 mg of KPS were added and stirred for another 24 hrs. The flask was cooled with dry ice to freeze, and then warmed up to RT. After 15 ml of 10% HNO<sub>3</sub> were added, the mixture was stirred at 90°C for 1.5 hrs, cooled to RT, filtered and washed with water 3 times to give white powder with some beige chunks. This was further dried in a vacuum oven at 100°C for 4 hrs to give 2.81 g of copolymer.

#### Examples 8:

p-CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was copolymerized with C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> using the following procedure:

A three-necked 100 mL flask, fitted with an N<sub>2</sub> inlet/outlet, a magnetic stirring bar and a thermocouple, was charged with 40 mL of deionized water and 3.8 mL of 20% ammonium perfluorooctanoate (C8)aqueous solution. The solution was bubbled with N<sub>2</sub> for 30 min. 5.0 g (14 mmol) g of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 0.63 g (4 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>5</sub> were added to the flask via a syringe under N<sub>2</sub> purge and ultrasonicated for 5 min. After heating to 55°C, 52 mg of potassium persulfate (KPS) in 2 mL of deionized water were added via a syringe and

the flask was kept at 55°C for 24 hrs. An additional 32 mg of KPS were added and the mixture was stirred over the weekend. The flask was cooled with dry ice to freeze, and then warmed up to RT. After 20 ml of 10% HNO<sub>3</sub> were added, the mixture was stirred at 90°C for 1.5 hrs, then

5 cooled to RT. The solids were slurried in 100 mL DI water three times to neutral of pH 6. 7.19 g of a white solid were recovered after air-drying overnight. The sample was further dried at 120°C under vacuum/N<sub>2</sub> overnight, recovering 4.00 g. of a beige particulate solid. <sup>19</sup>F NMR in THF solution indicated composition of

10 (CF<sub>2</sub>CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)<sub>7.4</sub>(CF<sub>2</sub>CFC<sub>6</sub>H<sub>5</sub>), Mw = 1.42x10<sup>5</sup>, Mn = 7.84x10<sup>3</sup>

Example 9:

CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was copolymerized with C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> @ 1:3 mole ratio using the following procedure:

15 A 250 mL three necked round bottomed flask, fitted with rubber septa, cold water condenser with a N<sub>2</sub> outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 50 mL of deionized water and 1.0 g of dodecylamine hydrochloride. The solution was bubbled with N<sub>2</sub> for 30 min, and then 2.8 g (7.86 mmol) g of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F

20 and 3.7 g (23.4 mmol) of C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> were added to the flask via a syringe under N<sub>2</sub> and ultrasonicated for 5 min. After heating to 55° C, 57 mg of KPS in 2 mL of water were added and the resulting mixture was stirred for 18 hrs, and then additional 15 mg of KPS were added. After being stirred for 33 hrs, the mixture was frozen with dry ice overnight and

25 warmed to RT. 50 ml of 10% HNO<sub>3</sub> were added, and the mixture was stirred at 90°C for 1.5 hrs. The resulting solids were too fine to filter and were recovered by centrifuging. The solids were slurried in 200 mL DI water two times and 150 mL 0.5N NaHCO<sub>3</sub> were added two times to result in a pH 6. Recovery was 2.79 g of a white solid after air-drying overnight.

30 Sample was further dried at 100°C under vacuum/N<sub>2</sub> overnight recovering 2.76 g. of solids. <sup>19</sup>F NMR indicated that composition was (CF<sub>2</sub>CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)(C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub>)<sub>2.66</sub>. +43.2 (m), -82.3 (m), -107.7 to -110.0, -112.5 (m), -170.5 to -179.7 (m) ppm. Mw = 3.04x10<sup>4</sup> and Mn = 3.69x10<sup>3</sup>

Example 10:

p-CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F was copolymerized with C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> using the following procedure:

A 250 mL three necked round bottomed flask, fitted with a rubber  
5 septa, cold water condenser with a N<sub>2</sub> outlet/inlet and bubbler; a magnetic stirring bar and thermocouple, was charged with 50 mL of deionized water and 1.0 g of dodecylamine hydrochloride. The solution was bubbled with N<sub>2</sub> for 30 min. 4.5 g (12.67 mmol) g of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 2.17 g (13.72 mmol) of C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> were added to the flask via a syringe  
10 under N<sub>2</sub>, and then ultrasonicated for 5 min. After heating to 50° C, 52 mg of KPS in 2 mL of water were added and the mixture was stirred for 25 hrs and an additional 15 mg of KPS in 2 mL of water were added. Stirring was continued over the weekend, and the mixture was frozen with dry ice overnight, and warmed to RT. 40 mL of saturated K<sub>2</sub>CO<sub>3</sub> solution were  
15 added, solids were isolated by centrifugation, washed with water and MeOH and dried in a vacuum oven to give 2.35 g of white polymer. <sup>19</sup>F NMR indicated that composition was (CF<sub>2</sub>CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)(C<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub>) and +43.2 (m), -82.3 (m), -107.7 to -110.0, -112.5 (m), -170.5 to -179.7 (m). Mw = 9.33x10<sup>3</sup> and Mn =  
20 1.17x10<sup>3</sup>.

Example 11:

p-CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and CF<sub>2</sub>=CFC<sub>6</sub>H<sub>5</sub>CF=CF<sub>2</sub> were copolymerized using the following procedure:

A 100 mL three necked round bottomed flask fitted with a rubber  
25 septa, cold water condenser with a N<sub>2</sub> outlet/inlet and bubbler; a magnetic stirring bar and thermocouple was charged with 40 mL of deionized water and 0.1 g of poly(difluoromethylene), alpha-fluoro-omega (2-sulfoethyl) ammonium salt (TLF-8927 fluorosurfactant, E. I. DuPont de Nemours and Co., Wilmington, DE). The solution was bubbled with N<sub>2</sub> for 30 min,  
30 followed by the addition of 7.22 g (20.27 mmol) of CF<sub>2</sub>=CFC<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 0.158 g (0.66mmol) of p-CF<sub>2</sub>=CF-C<sub>6</sub>H<sub>5</sub>-CF=CF<sub>2</sub> to the flask via a syringe under N<sub>2</sub>. After heating to 55° C, 52 mg of KPS in 2 mL of water were added and the mixture was stirred for 24 hrs. An additional 15 mg of KPS in 2 mL of water were added. After stirring for  
35 63 hrs, the mixture was frozen on dry ice overnight, and warmed to RT. 15 ml of 10% HNO<sub>3</sub> were added, and the mixture was stirred at 90° C for 1.5 hrs. After cooling to RT, the mixture was filtered and washed with

water thrice to give a whitish powder, which was dried in a vacuum oven at 100°C for 4 hrs to give 5.728 g. of a fine beige powder.

Example 12:

5  $\text{CF}_2=\text{CF}(\text{C}_6\text{H}_4)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and  $p\text{-CF}_2=\text{CF}(\text{C}_6\text{H}_5)\text{-CF}=\text{CF}_2$  were copolymerized using the following procedure:

A 100 mL three necked round bottomed flask fitted with a rubber septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple was charged with 40 mL of deionized water and 0.1 g of poly(difluoromethylene), alpha-fluoro-omega (2-sulfoethyl) ammonium salt (TLF-8927 fluorosurfactant, DuPont). The solution was  
10 bubbled with  $\text{N}_2$  for 30 min., followed by the addition of 7.22 g (20.27 mmol) of  $\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and 0.338 g (1.42 mmol) of  $p\text{-CF}_2=\text{CF-C}_6\text{H}_5\text{-CF}=\text{CF}_2$  to the flask via a syringe under  $\text{N}_2$ . After heating to 55° C, 52 mg of KPS in 2 mL of water were added, and the mixture was  
15 stirred for 24 hrs. An additional 15 mg of KPS in 2 mL of water were added. After continued stirring for 63 hrs, the mixture was frozen on dry ice overnight, and then warmed to RT. 15 ml of 10%  $\text{HNO}_3$  were added. The mixture was stirred at 90° C for 1.5 hrs, cooled to RT, filtered and washed with water thrice to give a whitish powder, that was dried in a  
20 vacuum oven at 100°C for 4 hrs to give 5.718 g. of a fine beige powder.

Example 13

$\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and  $p\text{-CF}_2=\text{CFC}_6\text{H}_5\text{CF}=\text{CF}_2$  were copolymerized using the following procedure:

A 100 mL three necked round bottomed flask fitted with a rubber  
25 septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple was charged with 40 mL of deionized water and 0.1 g of poly(difluoromethylene), alpha-fluoro-omega (2-sulfoethyl) ammonium salt (TLF-8927 fluorosurfactant, DuPont). The solution was bubbled with  $\text{N}_2$  for 30 minutes followed by the addition of 7.22 g (20.27  
30 mmol) of  $\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and 0.03 g (0.126mmol) of  $p\text{-CF}_2=\text{CF-C}_6\text{H}_5\text{-CF}=\text{CF}_2$  to the flask via a syringe under  $\text{N}_2$ . After heating to 55° C, 52 mg of KPS in 2 mL of water were added and the mixture was stirred for 24 hrs. An additional 15 mg of KPS in 2 mL of water were added. After continued stirring for 90 hrs, the mixture was frozen on dry  
35 ice overnight and warmed to RT. 15 ml of 10%  $\text{HNO}_3$  were added, the mixture was stirred at 90° C for 1.5 hrs, cooled to RT, filtered and washed with water thrice to give a whitish powder. This whitish powder was dried in a vacuum oven at 100°C for 4 hrs to give 5.94 g. of a fine beige powder.

Example 14:

$\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ ,  $\text{C}_6\text{H}_5\text{CF}=\text{CF}_2$  and p- $\text{CF}_2=\text{CFC}_6\text{H}_5\text{CF}=\text{CF}_2$  were copolymerized using the following procedure:

- A 100 mL three necked round bottomed flask fitted with a rubber  
5 septa, cold water condenser with a  $\text{N}_2$  outlet/inlet and bubbler; a magnetic stirring bar and thermocouple was charged with 25 mL of deionized water and 0.05 g of poly(difluoromethylene), alpha-fluoro-omega (2-sulfoethyl) ammonium salt (TLF-8927 fluorosurfactant; DuPont). The solution was bubbled with  $\text{N}_2$  for 30 min. followed by the addition of 4.1 g (11.5 mmol) of  
10  $\text{CF}_2=\text{CFC}_6\text{H}_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 1.28 g (8.1 mmol) of  $\text{C}_6\text{H}_5\text{CF}=\text{CF}_2$  and 0.07 g (0.29mmol) of p- $\text{CF}_2=\text{CF}-\text{C}_6\text{H}_5-\text{CF}=\text{CF}_2$  to the flask via a syringe under  $\text{N}_2$ . After heating to  $55^\circ\text{C}$ , 52 mg of KPS in 2 mL of water were added and the mixture was stirred for 24 hrs and an additional 15 mg of KPS in 2 mL of water were added. After continued stirring for 48 hrs, the mixture  
15 was frozen on dry ice overnight and warmed to RT. 15 ml of 10%  $\text{HNO}_3$  were added, the mixture was stirred at  $90^\circ\text{C}$  for 1.5 hrs, cooled to RT and centrifuged to give 2.14 g of yellow liquid and solid that was washed with toluene and dried in a vacuum oven at  $110^\circ\text{C}$  to give 1.15 g of white solid.

Example 15

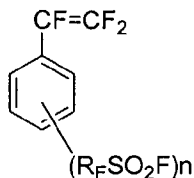
- 20 Copolymers were hydrolyzed using the following procedure:

The copolymer made in Example 7 was pressed into a thin film at  $260^\circ\text{C}$ . The film was immersed in 20% KOH in MeOH, water and DMSO in a ratio of 4:5:1 at room temperature for two hrs. After being washed with water thrice, the film was treated with 10%  $\text{HNO}_3$  at  $40^\circ\text{C}$  for 6 hrs, at  
25 room temperature overnight, and then treated with fresh 10%  $\text{HNO}_3$  again for two hrs. After being washed with de-ionized water, the film had conductivity of 240 mS/cm at  $80^\circ\text{C}$  and 95% relative humidity (RH) that was measured using the in-plane method.

CLAIMS

What is claimed is:

1. A monomer having the following structure:



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wherein R<sub>F</sub> is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine; and

- 10 n is 1 or 2.

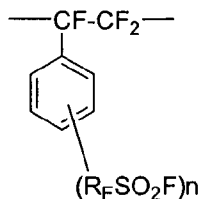
2. The monomer of claim 1 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>r</sub> wherein r = 1 to 20, (CF<sub>2</sub>CF<sub>2</sub>)<sub>r</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein r = 0 to 6, and CF(CF<sub>3</sub>)O)<sub>r</sub>CF<sub>2</sub>CF<sub>2</sub> wherein r = 1 to 8.

- 15 3. The monomer of claim 2 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>r</sub> wherein r = 1 to 8, (CF<sub>2</sub>CF<sub>2</sub>)<sub>r</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein r = 0 to 2, and CF(CF<sub>3</sub>)O)<sub>r</sub>CF<sub>2</sub>CF<sub>2</sub> wherein r = 1 to 2.

4. The monomer of claim 1 wherein n is 1.

5. A homopolymer having the following structure:

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wherein R<sub>F</sub> is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2.

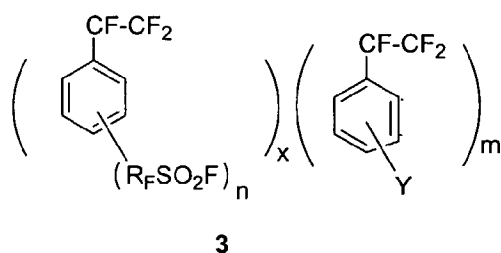
- 25 6. The homopolymer of claim 5 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>r</sub> wherein r = 1 to 20, (CF<sub>2</sub>CF<sub>2</sub>)<sub>r</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein r = 0 to 6, and CF(CF<sub>3</sub>)O)<sub>r</sub>CF<sub>2</sub>CF<sub>2</sub> wherein r = 1 to 8.

7. The homopolymer of claim 6 wherein  $R_F$  is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3)O)_rCF_2CF_2$  wherein  $r = 1$  to 2.

8. The homopolymer of claim 1 wherein  $n$  is 1.

5 9. A copolymer selected from the group consisting of:

(a) a copolymer having the structure:



10 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

15 n is 1 or 2,

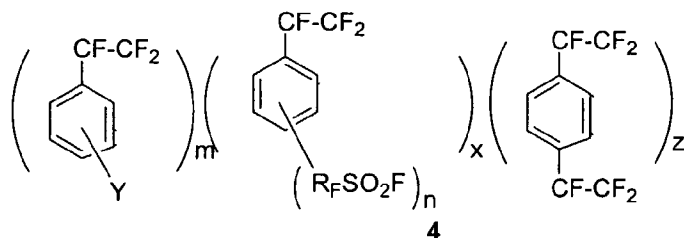
m and x are mole fractions wherein m is 0.01 to 0.99 and

x is 0.99 to 0.01; and

$x+m = 1$

(b) a copolymer having the structure:

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wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

25 Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01, and

z is 0.0001 to 0.10

5 m + x + z = 1.

10. The copolymer of claim 9 wherein  $R_F$  is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 8.

11. The copolymer of claim 10 wherein  $R_F$  is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 2.

12. The copolymer of claim 9 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms is selected from the group consisting of  $C_nF_{2n+1}$ , wherein  $n$  is 1 to 10; and  $C_nH_{2n+1}$ , wherein  $n$  is 1 to 10.

13. The copolymer of claim 9 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms is selected from the group consisting of  $CF_3(CF_2)_qO(CF_2CF_2)_q$  wherein  $q = 1$  to 5 and  $CF_3CF_2CF_2(OCF_2CF_2)_q$  wherein  $q = 1$  to 5.

14. The copolymer of claim 13 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected from the group consisting of  $CF_3(CF_2)_qOCF_2CF_2$  wherein  $q = 1$  to 2, and  $CF_3CF_2CF_2(OCF_2CF_2)_q$  wherein  $q = 1$  to 3.

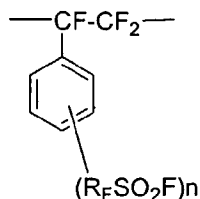
15. The copolymer of claim 14 wherein  $n$  is 1.

16. The copolymer of claim 9 wherein m and x are mole fractions, wherein m is 0.1 to 0.4; and x is 0.9 to 0.6 in structure 3.

17. The copolymer of claim 9 wherein m, x and z are mole fractions, wherein m is 0.2 to 0.6; x is 0.4 to 0.8; and z is 0.002 to 0.01 in structure 4.

18. A polymer electrolyte membrane prepared from a homopolymer or copolymer selected from the group consisting of:

(a) a homopolymer having the structure:



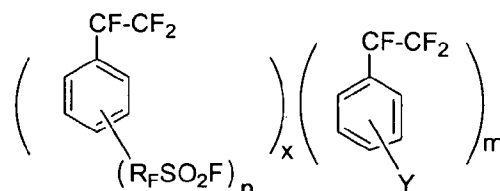


wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$n$  is 1 or 2;

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(b) a copolymer having the structure:



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wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

10         $Y$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

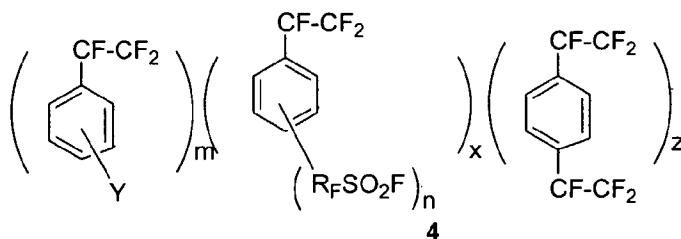
$n$  is 1 or 2,

15         $m$  and  $x$  are mole fractions wherein  $m$  is 0.01 to 0.99 and

$x$  is 0.99 to 0.01; and

$x+m = 1$ ; and

(c) a copolymer having the structure:



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wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$Y$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

25

m, x and z are mole fraction wherein m is 0.01 to 0.99,  
 x is 0.99 to 0.01, and  
 z is 0.0001 to 0.10

5 m + x + z = 1; and mixtures thereof.

19. The polymer electrolyte membrane of claim 18 further comprising a porous support.

20. The polymer electrolyte membrane of claim 18 wherein  $R_F$  in structure 2 is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 8.

21. The polymer electrolyte membrane of claim 20 wherein  $R_F$  in structure 2 is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 2.

22. The polymer electrolyte membrane of claim 18 wherein, in structure 2, n is 1.

23. The polymer electrolyte membrane of claim 18 wherein  $R_F$ , in structures 3 and 4, is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 8.

24. The polymer electrolyte membrane of claim 23 wherein  $R_F$  is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3O)_rCF_2CF_2$  wherein  $r = 1$  to 2.

25. The polymer electrolyte membrane of claim 18 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of  $C_nF_{2n+1}$ , wherein n is 1 to 10; and  $C_nH_{2n+1}$ , wherein n is 1 to 10.

26. The polymer electrolyte membrane of claim 18 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of  $CF_3(CF_2)_qO(CF_2CF_2)_q$  wherein q = 1 to 5 and  $CF_3CF_2CF_2(OCF_2CF_2)_q$  wherein q = 1 to 5.

27. The polymer electrolyte membrane of claim 26 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected

from the group consisting of  $\text{CF}_3(\text{CF}_2)_q\text{OCF}_2\text{CF}_2$  wherein  $q = 1$  to  $2$ , and  $\text{CF}_3\text{CF}_2\text{CF}_2(\text{OCF}_2\text{CF}_2)_q$  wherein  $q = 1$  to  $3$ .

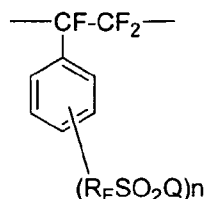
28. The polymer electrolyte membrane of claim 18 wherein  $n$ , in structures **3** and **4**, is 1.

5 29. The polymer electrolyte membrane of claim 18 wherein  $m$  and  $x$  are mole fractions, wherein  $m$  is 0.1 to 0.4; and  $x$  is 0.9 to 0.6 in structure **3**.

30. The polymer electrolyte membrane of claim 18 wherein  $m$ ,  $x$  and  $z$  are mole fractions, wherein  $m$  is 0.2 to 0.6;  $x$  is 0.4 to 0.8; and  $z$  is 0.002 to 0.01 in structure **4**.

31. A polymer electrolyte membrane selected from the group consisting of:

(a) a membrane having the chemical structure:



5

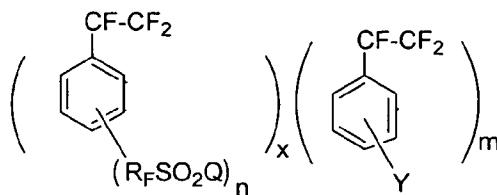
15 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$Q = \text{OM}, \text{OH}, \text{NHSO}_2\text{R}_F$ , wherein  $M = \text{Li}^+, \text{Na}, \text{K}$  or  $\text{Cs}$ ,

$n = 1$  or  $2$ ;

(b) a membrane having the chemical structure:

20



6

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$Y$  is  $\text{H}$ ; halogen such as  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{F}$  or  $\text{I}$ ; linear or branched

25 perfluoroalkyl groups, wherein the alkyl group comprises  $\text{C}1$  to  $\text{C}10$  carbon

atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine,  
and wherein the alkyl group comprises C1 to C10 carbon atoms,

$Q = OM, OH, NHSO_2R_F$ , wherein  $M = Li^+, Na^+, K^+$  or  $Cs^+$ ,

$n$  is 1 or 2,

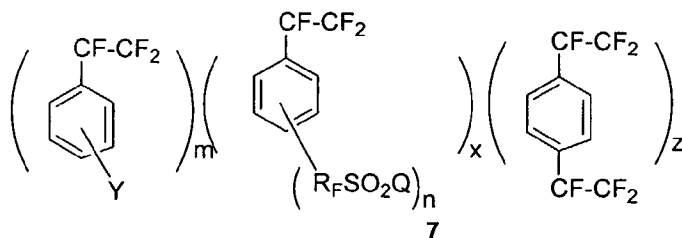
5  $m$  and  $x$  are mole fractions wherein  $m$  is 0 to 0.99,

$x$  is 1 to 0.001, and

$x + m = 1$ ; and

(c) a membrane having the chemical structure:

10



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally  
containing oxygen or chlorine,

$Y$  is H; halogen such as Cl, Br, F or I; linear or branched

15 perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon  
atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine,  
and wherein the alkyl group comprises C1 to C10 carbon atoms,

$Q = OM, OH, NHSO_2R_F$ , wherein  $M = Li^+, Na^+, K^+$  or  $Cs^+$ ,

$n$  is 1 or 2,

20  $m$ ,  $x$  and  $z$  are mole fractions wherein  $m$  is 0.01 to 0.99 ,

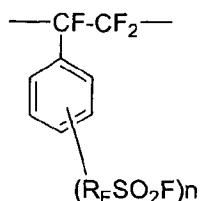
$x$  is 0.99 to 0.01,

$z$  is 0.0001 to 0.10, and

$m + x + z = 1$

32. A membrane electrode assembly comprising a polymer  
25 electrolyte membrane, having a first surface and a second surface,  
wherein the membrane is prepared from a homopolymer or copolymer  
selected from the group consisting of:

(a) a homopolymer having the structure:

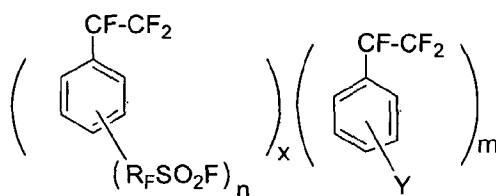


2

wherein  $\text{R}_\text{F}$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

5  $n$  is 1 or 2;

(b) a copolymer having the structure:



3

wherein  $\text{R}_\text{F}$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

10  $\text{Y}$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

15  $n$  is 1 or 2,

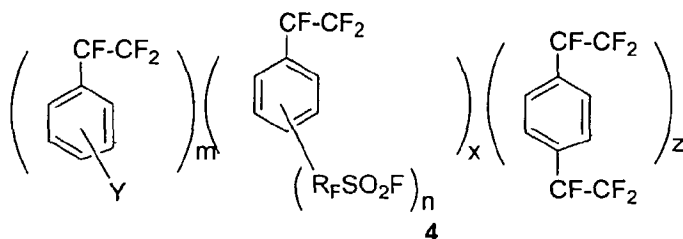
$m$  and  $x$  are mole fractions wherein  $m$  is 0.01 to 0.99,

$x$  is 0.99 to 0.01; and

$x+m = 1$ ; and

(c) a copolymer having the structure:

20



4

wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01, and

z is 0.0001 to 0.10

$m + x + z = 1$ ; and mixtures thereof.

33. The membrane electrode assembly of claim 32 wherein the polymer electrolyte membrane further comprises a porous support.

34. The membrane electrode assembly of claim 32 further comprising at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the membrane.

35. The membrane electrode assembly of claim 34 further comprising at least one gas diffusion backing present on the at least one electrode on the side away from the polymer electrolyte membrane.

36. The membrane electrode assembly of claim 32 further comprising a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

37. The membrane electrode assembly of claim 32 wherein  $R_F$  in structure **2** is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6, and  $CF(CF_3)O_rCF_2CF_2$  wherein  $r = 1$  to 8.

38. The membrane electrode assembly of claim 37 wherein  $R_F$  in structure **2** is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3)O_rCF_2CF_2$  wherein  $r = 1$  to 2.

39. The membrane electrode assembly of claim 32 wherein n, in structure **2**, is 1.

40. The membrane electrode assembly of claim 32 wherein  $R_F$ , in structures **3** and **4**, is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 20,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 6, and  $CF(CF_3)O_rCF_2CF_2$  wherein  $r = 1$  to 8.

41. The membrane electrode assembly of claim 40 wherein  $R_F$  is selected from the group consisting of  $(CF_2)_r$  wherein  $r = 1$  to 8,  $(CF_2CF_2)_rOCF_2CF_2$  wherein  $r = 0$  to 2, and  $CF(CF_3)O)_rCF_2CF_2$  wherein  $r = 1$  to 2.

42. The membrane electrode assembly of claim 32 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, in structures **3** and **4**, is selected from the group consisting of  $C_nF_{2n+1}$ , wherein  $n$  is 1 to 10; and  $C_nH_{2n+1}$ , wherein  $n$  is 1 to 10.

43. The membrane electrode assembly of claim 32 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, in structures **3** and **4**, is selected from the group consisting of  $CF_3(CF_2)_qO(CF_2CF_2)_q$  wherein  $q = 1$  to 5 and  $CF_3CF_2CF_2(OCFCF_3)_q$  wherein  $q = 1$  to 5.

44. The membrane electrode assembly of claim 43 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected from the group consisting of  $CF_3(CF_2)_qOCF_2CF_2$  wherein  $q = 1$  to 2, and  $CF_3CF_2CF_2(OCFCF_3)_q$  wherein  $q = 1$  to 3.

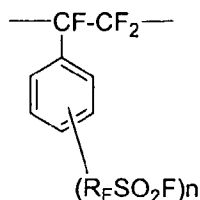
45. The membrane electrode assembly of claim 32 wherein  $n$ , in structures **3** and **4**, is 1.

46. The membrane electrode assembly of claim 32 wherein  $m$  and  $x$  are mole fractions, wherein  $m$  is 0.1 to 0.4; and  $x$  is 0.9 to 0.6 in structure **3**.

47. The polymer electrolyte membrane of claim 46 wherein  $m$ ,  $x$  and  $z$  are mole fractions, wherein  $m$  is 0.2 to 0.6;  $x$  is 0.4 to 0.8; and  $z$  is 0.002 to 0.01 in structure **4**.

48. A electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the membrane is prepared from a homopolymer or copolymer selected from the group consisting of:

(a) a homopolymer having the structure:

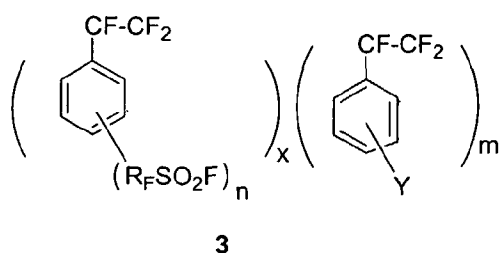


wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$n$  is 1 or 2;

5

(b) a copolymer having the structure:



10 wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

$Y$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine,

15 and wherein the alkyl group comprises C1 to C10 carbon atoms,

$n$  is 1 or 2,

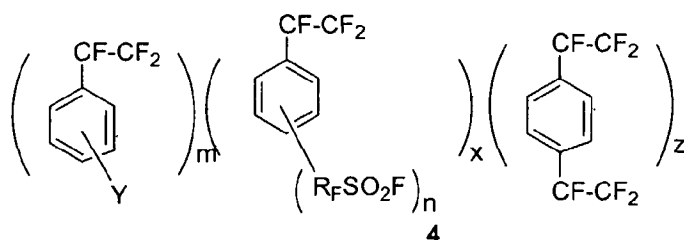
$m$  and  $x$  are mole fractions wherein  $m$  is 0.01 to 0.99,

$x$  is 0.99 to 0.01,

$x+m = 1$ , and

20

(c) a copolymer having the structure:



wherein  $R_F$  is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

25

$Y$  is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon



atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine,  
and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

5 x is 0.99 to 0.01,

z is 0.0001 to 0.10, and

$m + x + z = 1$ ; and mixtures thereof.

49. The electrochemical cell of claim 48 wherein the  
10 electrochemical cell is a fuel cell.

50. The fuel cell of claim 49 wherein the polymer electrolyte  
membrane further comprises a porous support.

51. The fuel cell of claim 49 further comprising at least one  
electrode prepared from an electrocatalyst containing composition present  
15 on the first and second surfaces of the polymer electrolyte membrane.

52. The fuel cell of claim 51 further comprising at least one gas  
diffusion backing.

53. The fuel cell of claim 49 further comprising a gas diffusion  
electrode present on the first and second surfaces of the membrane,  
20 wherein the gas diffusion electrode comprises a gas diffusion backing and  
an electrode prepared from an electrocatalyst containing composition.

54. The fuel cell of claim 51 further comprising a means for  
delivering a fuel to the anode, a means for delivering oxygen to the  
cathode, a means for connecting the anode and cathode to an external  
25 electrical load, hydrogen or methanol in the liquid or gaseous state in  
contact with the anode, and oxygen in contact with the cathode.

55. The fuel cell of claim 53 further comprising a means for  
delivering a fuel to the anode, a means for delivering oxygen to the  
cathode, a means for connecting the anode and cathode to an external  
30 electrical load, hydrogen or methanol in the liquid or gaseous state in  
contact with the anode, and oxygen in contact with the cathode.

56. The fuel cell of claim 49 wherein the fuel is an alcohol or ether.

57. The fuel cell of claim 56 wherein the fuel is methanol.

58. The fuel cell of claim 49 wherein the fuel is hydrogen.

35

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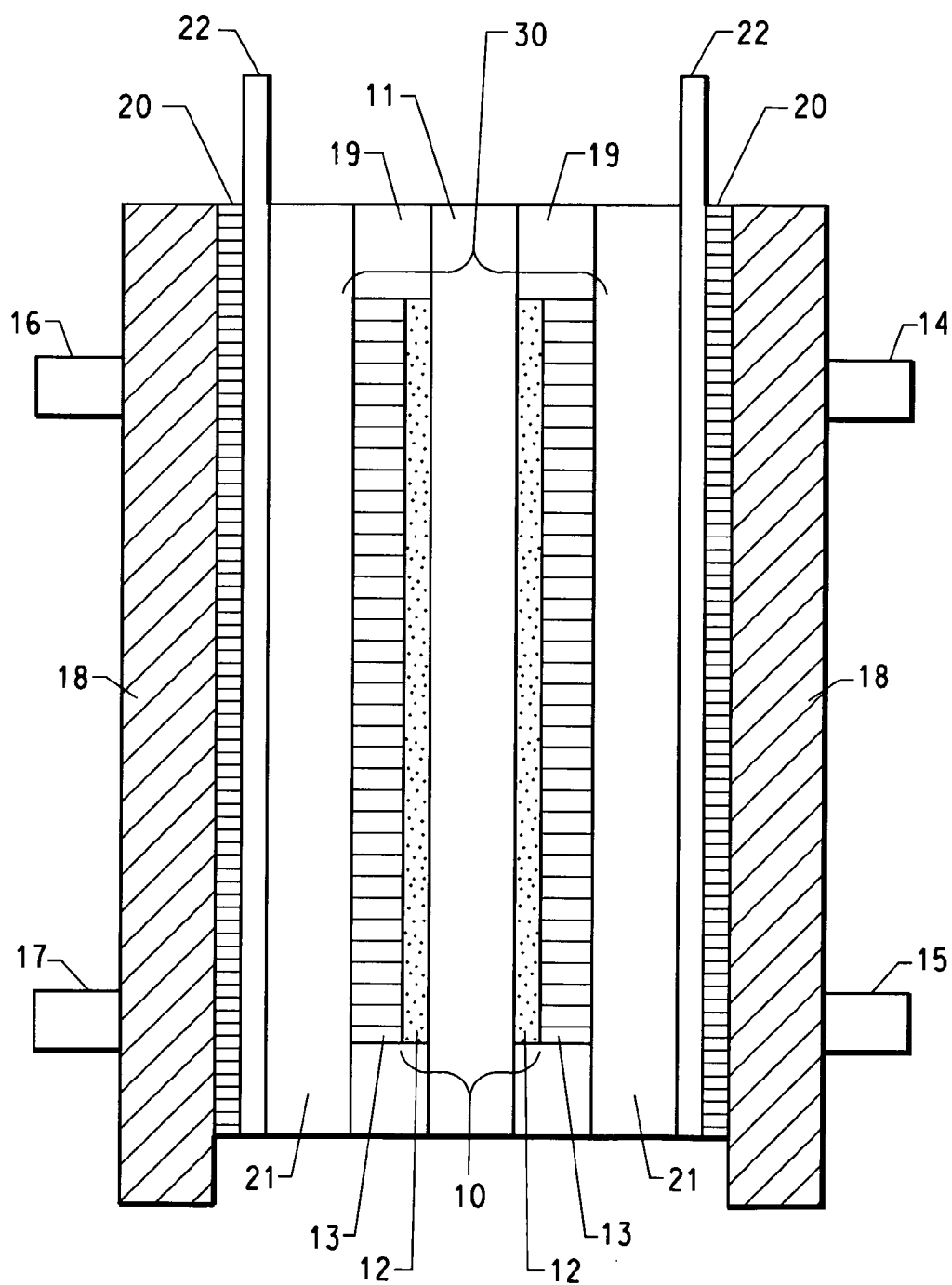


FIG. 1

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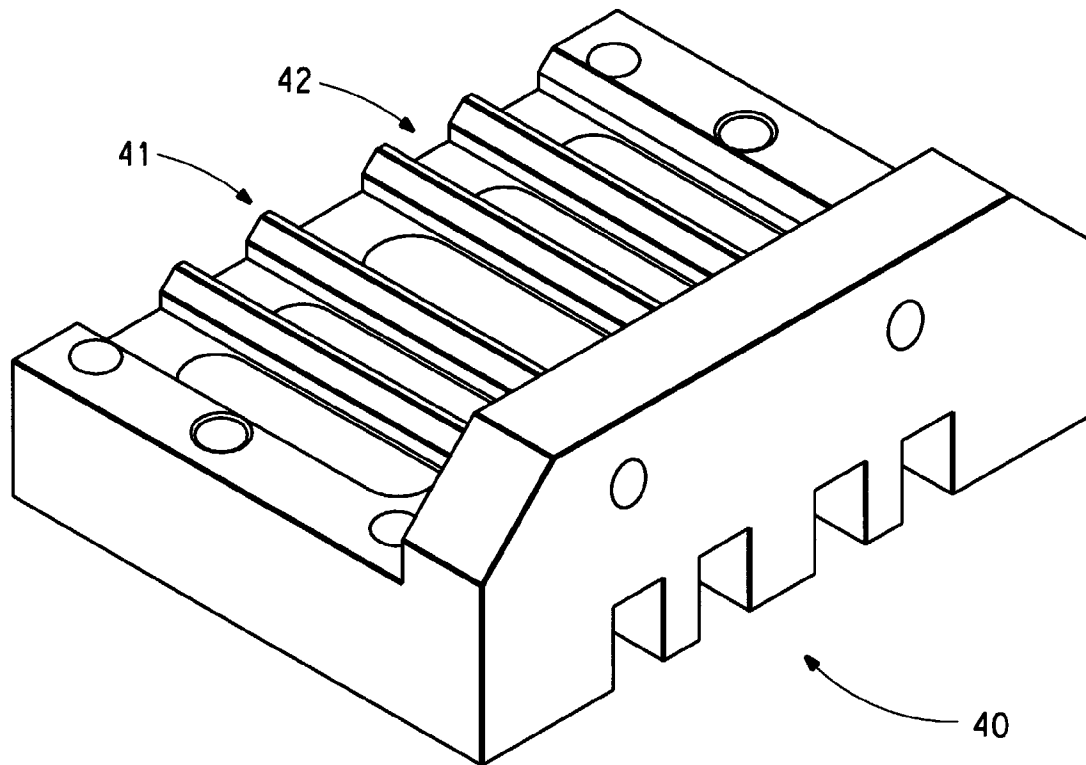


FIG. 2

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/020706

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C309/82 C08F14/18 H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08F H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	DATABASE CAPLUS CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; XP002303652 Database accession no. 2004:209841	1-4, 9-58
Y	abstract  & CN 1 349 962 A (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY) 22 May 2002 (2002-05-22)	5-8, 18-58
Y	WO 97/25369 A (BALLARD POWER SYSTEMS) 17 July 1997 (1997-07-17) claims 8,9; example 6  ----- -/-	5-8, 18-58



Further documents are listed in the continuation of box C



Patent family members are listed in annex

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

7 December 2004

Date of mailing of the international search report

21/12/2004

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/020706

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98/20573 A (DU PONT DE NEMOURS) 14 May 1998 (1998-05-14)  claim 1; examples -----	1,5,9, 18,31, 32,48
A	WO 96/39379 A (BALLARD POWER SYSTEMS) 12 December 1996 (1996-12-12)  claims 1,4,16,18; examples -----	1,5,9, 18,31, 32,48
A	EP 1 170 310 A (SAMSUNG ELECTRONICS) 9 January 2002 (2002-01-09)  page 8, line 11 - line 41; claims 1,7,8; figure 2 -----	1,5,9, 18,31, 32,48

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/020706

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 1349962	A	22-05-2002	NONE	
WO 9725369	A	17-07-1997	US 5834523 A	10-11-1998
			AT 194366 T	15-07-2000
			AU 704923 B2	06-05-1999
			AU 1187297 A	01-08-1997
			CA 2240495 A1	17-07-1997
			WO 9725369 A1	17-07-1997
			DE 69702442 D1	10-08-2000
			DE 69702442 T2	08-02-2001
			EP 0882088 A1	09-12-1998
			JP 2000502625 T	07-03-2000
			US 2002161061 A1	31-10-2002
			US 5985942 A	16-11-1999
			US 6258861 B1	10-07-2001
			US 2001056128 A1	27-12-2001
WO 9820573	A	14-05-1998	AU 5099498 A	29-05-1998
			DE 69728053 D1	15-04-2004
			DE 69728053 T2	21-10-2004
			EP 0938755 A1	01-09-1999
			JP 2001503910 T	21-03-2001
			KR 2000052944 A	25-08-2000
			WO 9820573 A1	14-05-1998
			US 6033804 A	07-03-2000
WO 9639379	A	12-12-1996	US 5602185 A	11-02-1997
			AU 709356 B2	26-08-1999
			AU 5889396 A	24-12-1996
			CA 2221813 A1	12-12-1996
			WO 9639379 A1	12-12-1996
			DE 69610322 D1	19-10-2000
			DE 69610322 T2	26-04-2001
			EP 0848702 A1	24-06-1998
			JP 11506149 T	02-06-1999
			US 5684192 A	04-11-1997
			US 5773480 A	30-06-1998
EP 1170310	A	09-01-2002	KR 2002004065 A	16-01-2002
			EP 1170310 A2	09-01-2002
			US 2004202913 A1	14-10-2004
			US 2002015874 A1	07-02-2002